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(54) SILICONE-BASED POLYMER AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a copolymer consisting of a saturated hydrocarbon-based polymer segment and a silicone-based polymer segment, and improved in coatability without significantly lowering its weathering resistance and mechanical properties.
SOLUTION: This copolymer is obtained by reacting (A) a saturated hydrocarbon-based polymer component, preferably a polymer component having an alkenyl or vinyl group with (B) a silicone-based polymer component, wherein the component B is a silicone-based polymer having a hydrosilyl group, preferably a polymer shown by the formula (R is a 1-20C monovalent organic group; (n) is an integer of 2 or more; (w) is the number of cyclic structures in the silicone-based polymer; (x) and (y) are each 2 or more, but (x)+(y)=2(n)+2-2(w)).

$$Si_nO_{n-1+w}R_xH_y$$

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]A copolymer which consists of a saturated hydrocarbon system polymer component and a silicone series polymer component.
[Claim 2]The copolymer according to claim 1 obtained by a reaction with a silicone series polymer characterized by comprising the following.
A saturated hydrocarbon system polymer which has an alkenyl group.
A hydrosilyl group.

[Claim 3]The copolymer according to claim 1 obtained by a reaction with a silicone series polymer characterized by comprising the following.
A saturated hydrocarbon system polymer which has a vinyl group at the end.
A hydrosilyl group.

[Claim 4]A silicone series polymer which has a hydrosilyl group is formula (1):$Si_nO_{n-1+w}R_xH_y$ (1).
the copolymer according to claim 1 to 3, wherein n which may be the same at a univalent organic group of the carbon numbers 1-20 as for R, or may differ among [type is expressed with two or more integers and both the number of cyclic structures in a silicone series polymer, x, and y are expressed with zero or more integer, however x+y=2n+2-2w] as for w.
[Claim 5]A coating method using as a polymer a hardened material using a copolymer which consists of a saturated hydrocarbon system polymer component and a silicone series polymer component, or this copolymer in a method of painting a paint on the surface of a hardened material using a silicone series polymer or a silicone series polymer.

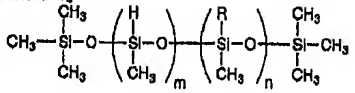
[Translation done.]

DETAILED DESCRIPTION

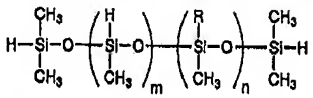
[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the copolymer which consists of a saturated hydrocarbon system polymer component and a silicone series polymer component.
[0002]
[Description of the Prior Art]Since the weatherability and mechanical characteristic are good, the silicone series polymer is widely used as raw materials, such as a sealing material and a coating material. However, generally, since the paintwork of a silicone series polymer is not so good, silicone system sealing compounds are not used for the portion to be painted.
[0003]
[Problem(s) to be Solved by the Invention]There is a technical problem of this invention in improving the paintwork of a silicone series polymer, without reducing weatherability and a mechanical characteristic greatly.
[0004]
[Means for Solving the Problem]A technical problem of this invention is solved with a copolymer which consists of a silicone series polymer component and a saturated hydrocarbon system polymer component. A copolymer from which this invention is furthermore obtained by the reaction of a saturated hydrocarbon system polymer which has an alkenyl group, and a silicone series polymer which has a hydrosilyl group, It is related with a copolymer obtained by the reaction of a saturated hydrocarbon system polymer which has a vinyl group at the end, and a silicone series polymer which has a hydrosilyl group. As for this invention, a silicone series polymer which has a hydrosilyl group is formula (1):$Si_nO_{n-1+w}R_xH_y$ (1).

both the number of cyclic structures in a silicone series polymer, x, and y are related with the above-mentioned copolymer, wherein n which may be the same at a univalent organic group of the carbon numbers 1-20 as for R, or may differ among [type is expressed with two or more integers and w is expressed with zero or more integer, however x+y=2n+2-2w].
[0005]
[Embodiment of the Invention]The silicone series polymer component in the copolymer of this invention means the polymer component which has a polysiloxane principal chain skeleton, and, as for the number average molecular weight (the GPC method, polystyrene conversion) of this silicone series polymer component, it is preferred that it is 300 to about 400000.
[0006]In the copolymer of this invention, a saturated hydrocarbon system polymer component means the polymer component which does not contain substantially carbon-carbon unsaturated bonds other than an aromatic ring in a main chain, and, as for the number average molecular weight (the GPC method, polystyrene conversion) of this saturated hydrocarbon system polymer, it is preferred that it is 300 to about 100000. The saturated hydrocarbon system polymer component is excellent in weatherability, and does not reduce the weatherability of a silicone series polymer component.
[0007]The copolymers of this invention are conventionally publicly known copolymers, such as a block copolymer and a graft copolymer, for example. As for the number average molecular weight (the GPC method, polystyrene conversion) of the copolymer of this invention, it is preferred that it is 500 to about 500000, and it is especially preferred that it is what is 1000 to about 300000. The copolymer of this invention can manufacture a silicone series polymer and a saturated hydrocarbon system

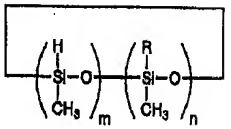
polymer as a raw material. For example, it can obtain by making the saturated hydrocarbon system polymer which has an alkenyl group, and the silicone series polymer which has a hydrosilyl group react.
[0008]The silicone series polymer which the silicone series polymer refers to the polymer which has a polysiloxane principal chain skeleton, and has a hydrosilyl group says the silicone series polymer containing at least one hydrosilyl group to intramolecular. Here, one SiH group is put in hydrosilyl group 1 piece. Therefore, when two hydrogen atoms have combined with the same Si, it may be hydrosilyl group 2 piece.
[0009]As an example of the silicone series polymer which has a hydrosilyl group, it is formula (1):$Si_nO_{n-1+w}R_xH_y$ (1).
both the number of the cyclic structures in a silicone series polymer, x, and y can mention the polymer by which n which may be the same at the univalent organic group of the carbon numbers 1-20 as for R, or may differ among [type is expressed with two or more integers, and w is expressed with zero or more integer, however x+y=2n+2-2w]. Although hydrocarbon groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, a phenyl group, 2-phenylethyl group, and a 2-methyl-2-phenylethyl group, are mentioned and things are made as R in a formula (1), A methyl group, a phenyl group, 2-phenylethyl group, and a 2-methyl-2-phenylethyl group are preferred.
[0010]If the example of the silicone series polymer which has a hydrosilyl group is shown concretely,
[0011]
[Formula 1]



（1 0≦m+n、1≦m≦5、0≦n、Rとしては炭素数2～20の炭化水素基で1個以上のフェニル基を含有してもよい。）



（1 0≦m+n、1≦m≦5、0≦n、Rとしては炭素数2～20の炭化水素基で1個以上のフェニル基を含有してもよい。）



（2≦m+n、1≦m≦5、0≦n、Rとしては炭素数2～20の炭化水素基で1個以上のフェニル基を含有してもよい。）

[0012]It comes out and what that is expressed is [being a chain and] annular is mentioned. As for the number average molecular weight (the GPC method, polystyrene conversion) of said silicone series polymer, it is preferred that it is 300 to about 400000, and what is 1000 to about 200000 is especially preferred. In this invention, although there should just be the one or more number of the hydrosilyl group contained in the silicone series polymer which has a hydrosilyl group, it is preferred that they are 1-10 pieces.
[0013]A saturated hydrocarbon system polymer is a concept meaning the polymer which does not contain substantially carbon-carbon unsaturated bonds other than an aromatic ring in a main chain, and that as used in this invention means that the repeating unit which constitutes a main chain comprises saturated hydrocarbon. The main chain of a saturated hydrocarbon system polymer shows the portion except the molecular chain terminals or the side chain in a polymer. Therefore, in this invention, if it does not have a carbon-carbon double bond except an aromatic ring other than an end or a side chain even when it has an alkenyl group in a molecular terminal or a side chain, it will

become a saturated hydrocarbon system polymer. An alkenyl group means the basis which has a carbon-carbon double bond which has activity to a hydrosilylation reaction. As an alkenyl group, for example A vinyl group, an allyl group, a methylvinyl group, Although cyclic unsaturated hydrocarbon groups, such as aliphatic-unsaturated-hydrocarbon groups, such as a propenyl group, a butenyl group, a pentenyl group, and a hexenyl group, a cyclopropenyl group, a cyclo butenyl group, a cyclopentenyl group, and a cyclohexenyl group, are mentioned, especially a vinyl group and an allyl group are preferred. As for a saturated hydrocarbon system polymer, in this invention, it is desirable to have 1-10 alkenyl groups in the molecular terminal or the side chain. A saturated hydrocarbon system polymer (1) ethylene, propylene, 1-butene, . Polymerize the olefinic compound of the carbon numbers 1-6, such as isobutylene, as a main monomer. (2) Although it can obtain by the method of making diene series, such as butadiene and isoprene, homopolymerize, or hydrogenating after carrying out copolymerization of the above-mentioned olefinic compound and the diene series, It is desirable that it is the isobutylene system polymer from a point of being able to increase the number of end functional groups, hydrogenation polybutadiene system polymer, or hydrogenation polyisoprene system polymer which is easy to introduce a functional group into an end and which is easy to carry out molecular weight control.

[0014]As for said isobutylene system polymer, all the monomeric units may be formed from an isobutylene unit, it is [in an isobutylene system polymer] desirable, and a monomeric unit which has isobutylene and copolymeric may be especially contained in 20% or less of range preferably 30% or less still more preferably below 50% (% of the weight and the following -- the same). As such a monomer component, an olefin of the carbon numbers 4-12, vinyl ether, an aromatic vinyl compound, vinylsilane, and arylsilane are mentioned, for example. As an example of such a copolymer component, for example 1-butene, 2-butene, A 2-methyl-1-butene, a 3-methyl-1-butene, a pentene, 4-methyl-1-pentene, A hexene, vinylcyclohexane, the methyl vinyl ether, ethyl vinyl ether, Isobutylvinyl ether, styrene, alpha-methylstyrene, dimethylstyrene, p-t-butoxystyrene, p-hexenyloxy styrene, p-allyloxy styrene, p-hydroxystyrene, beta-pinene, indene, vinyldimethylmethoxysilane, Vinyl trimethylsilane, divinyl dimethoxysilane, divinyl dimethylsilane, 1,3-divinyl- 1,1,3,3-tetramethyl disiloxane, TORIBI nil methylsilane, A tetravinyl silane, allyldimethyl methoxysilane, allyl trimethylsilane, diaryl dimethoxysilane, diaryl dimethylsilane, gamma-methacryloyl oxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl methyl dimethoxysilane, etc. are mentioned.

[0015]Other monomeric units other than a monomeric unit used as the main ingredients as well as a case of the above-mentioned isobutylene system polymer may be made to contain also in said hydrogenation polybutadiene system polymer or other saturated hydrocarbon system polymers. To a saturated hydrocarbon system polymer, the purpose of this invention in the range attained Butadiene, A little monomeric units in which an after-polymerization double bond like a polyene compound like isoprene, 1,13-tetradecadiene, 1,9-decadiene, and 1,5-hexadiene remains may be made to contain in 10% or less of range preferably.

[0016]said saturated hydrocarbon system polymer -- desirable -- a number average molecular weight (the GPC method.) of an isobutylene system polymer, hydrogenation polyisoprene, or a hydrogenation polybutadiene system polymer As for polystyrene conversion, it is preferred that it is 300 to about 100000, and it is especially preferred from points, such as the ease of dealing with it, that they are a liquid object which is 1000 to about 40000, and a thing which has mobility.

[0017]A manufacturing method of said saturated hydrocarbon system polymer is indicated to JP,8-53514,A, JP,6-291935,A, and JP,6-287241,A. When making a saturated hydrocarbon system polymer which has an alkenyl group, and a silicone series polymer which has a hydrosilyl group react, as for a ratio of an alkenyl group and a hydrosilyl group, 0.2-5.0 are preferred, and also 0.4-2.5 are more preferred. When using this reaction, it is possible to obtain a copolymer which has a hydrosilyl group or an alkenyl group at the end etc. For example, in a reaction of a silicone series polymer and a saturated hydrocarbon system polymer, when referred to as number of mols >1 of the number of mols / alkenyl group of a hydrosilyl group, a copolymer which has a hydrosilyl group at the end can be obtained. The copolymer which has a hydrosilyl group at the end can obtain a hardened material by a hydrosilylation reaction with a compound or a polymer which has two or more alkenyl groups.

[0018]In the case of number of mols <1 of the number of mols / alkenyl group of a hydrosilyl group, a copolymer which has an alkenyl group at the end etc. can be obtained. The copolymer which has an alkenyl group at the end etc. can obtain a hardened material by performing a hydrosilylation reaction

with a compound or a polymer which has two or more hydrosilyl groups. It is possible by adjusting a value of the number of mols of the number of mols / alkenyl group of a hydrosilyl group in this invention to set up a molecular weight of a copolymer arbitrarily. In the case of number of mols =1 of the number of mols / alkenyl group of a hydrosilyl group, in a theory top, a molecular weight can obtain a large copolymer infinitely.

[0019]A hydrosilylation catalyst may be used when performing a reaction of a saturated hydrocarbon system polymer which has an alkenyl group, and a silicone series polymer which has a hydrosilyl group. About a hydrosilylation catalyst, there is no restriction in particular and a publicly known thing can be used conventionally. a thing; platinum-vinyl siloxane complex which made carriers, such as chloroplatinic acid, a simple substance of platinum, alumina, silica, and carbon black, support solid platinum when illustrating concretely -- [-- for example, $Pt_n(ViMe_2SiOSiMe_2Vi)_n$ and Pt [(MeViSiO)$_4$] a $_m$]; platinum-phosphine complex {$Pt(PPh_3)_4$, $Pt(PBu_3)_4$}; platinum-phosphite complex -- [-- for example, Pt [for example,] [$P(OPh)_3$] $_4$, Pt [$P(OBu)_3$] $_4$ (the inside of a formula, and Me -- a methyl group and Bu -- a butyl group and Vi -- a vinyl group.) Pt(acac) $_2$ to which Ph expresses a phenyl group and n and m express an integer, A platinum-hydrocarbon complex indicated in Ashby's (Ashby) United States patent 3159601st, and the No. 3159662 specification and U.S. Pat. No. 3220972 of ******- (Lamoreaux) A platinum alcoholate catalyst indicated in a specification is also mentioned.

[0020]As an example of catalysts other than a platinum compound, $RhCl(PPh_3)_3$, $RhCl_3$, $Rh/aluminum_2O_3$, $RuCl_3$, $IrCl_3$, $FeCl_3$, $AlCl_3$, $PdCl_2and2H_2O$, $NiCl_2$, $TiCl_4$, etc. are mentioned. These catalysts may be used alone and may be used together two or more sorts. Chloroplatinic acid, a platinum-olefin complex, a platinum-vinyl siloxane complex, Pt(acac) $_2$, etc. are preferred from a point of catalytic activity. Although there is no restriction in particular as a catalyst amount, it is good to use in the range of 10^{-1} - 10^{-8}mol to 1 mol of alkenyl groups in a saturated hydrocarbon system polymer. It is good to use in the range of 10^{-2} - 10^{-6}mol preferably. It is better for a hydrosilylation catalyst to be expensive generally and to be corrosiveness, and for more than 10^{-1} mol not to use, since hydrogen gas is generated in large quantities and a hardened material may foam.

[0021]Although a copolymer manufactured in this invention has a block copolymer, a preferred graft copolymer, etc., for example, it is possible for there to be no restriction in particular in the structure, and to manufacture a publicly known copolymer arbitrarily conventionally. Although it may be used for various uses as it is, if needed, a copolymer of this invention may be used as vulcanization or a hardenability constituent which can carry out crosslinking reaction, and may be used. When using a hardenability constituent, it can harden with a curing method of the usual silicone series polymer, etc. A copolymer which has at the end etc. vulcanization using (1), for example, sulfur, peroxide, etc. as a method of obtaining a cured body, and (2) hydrosilyl group, A copolymer which has at the end etc. a hardening reaction by a hydrosilylation reaction with a compound or a polymer which has two or more alkenyl groups, and (3) alkenyl groups, Although hardening reaction ** by a hydrosilylation reaction with arbitrary compounds or polymers which have two or more hydrosilyl groups is mentioned, it is not limited to these.

[0022]A copolymer of this invention or its hardened material can be used conveniently for a use of a sealing material, a coating material, various Plastic solids, a sealing agent, an electrical insulation material, adhesives, a binder, a paint, a vibroisolating material, a potting material, medical-application rubber, a structural sealing material, a sealing material for multiple glass, etc. As a paint at the time of painting a copolymer of this invention, For example, a paint of the hardenability of an oil paint, distemper, lacquer, a varnish, enamel, rubber-base paint, etc. or nonhardening can be used, for example, a paint of acrylic, an alkyd system, a polyester system, an epoxy system, a phenol resin system, and an acrylic silicon system, etc. can be used.

[0023]Although this invention is explained still in detail below based on an example, this invention does not receive restriction at all by these.

[0024]

[Example]

The polymer A(an analytical value is shown in Table 1) 5.49g (amount of vinyl groups 2.02mmol) in

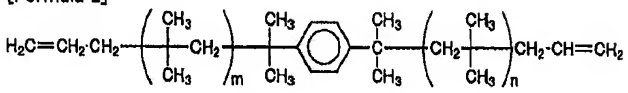
which structure is shown at the following compounded by the method given in JP,8-53514,A in the reaction flask of 130 ml of examples, The polymer B (an analytical value is shown in Table 1), 3.98 g (Si-H radical weight 1.01mmol), and 5 ml of heptane were added.

[0025]further -- as a catalyst --- a bis(1,3-divinyl- 1, 1, and 3, 3-tetramethyl disiloxane)platinum complex catalyst ($8.3x10^{-5}$mmol/mul.) After mixing uniformly 4.9micro of xylene solution I (the amount of platinum to the number of mols of the amount of vinyl groups of the polymer A: $5x10^{-4}$ equivalent), it stirred at 70 ** for 6 hours. Then, volatile matter content was distilled off with decompression, the block copolymer 9.2g was isolated, and GPC and 1 H-NMR estimated the characteristic. A result is shown in Table 2.

[0026]After adding the polyorgano hydrogen siloxane and the platinum system catalyst to the block copolymer obtained in example 2 Example 1 and mixing, the hardened material was created by heating. When acrylic distemper was applied to this hardened material, the paintwork of this block copolymer was good compared with the silicone series polymer.

[0027]

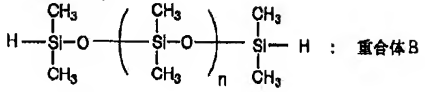
[Formula 2]



（m，nは整数） ： 重合体A

[0028]

[Formula 3]



： 重合体B

（nは整数）

[0029]

[Table 1]

	Mn(GPC)	Fn(ビニル)	Fn(SiH)
重合体A	5400	2.0	-
重合体B	7900	-	2.0

Fn(ビニル)：重合体A1分子中に含まれるビニル基の数の平均値

Fn(SiH)：重合体B1分子中に含まれるヒドロシリル基(SiH基)の数の平均値

[0030]

[Table 2]

	Mn	Fn(ビニル)	Fn(SiH)
実施例1	19800	1.8	0.1

[0031]

[Effect of the Invention]If the method of this invention is followed, it is possible to obtain the resin in which the paintwork of a silicone series polymer has been improved.

[Translation done.]